MS.17.5

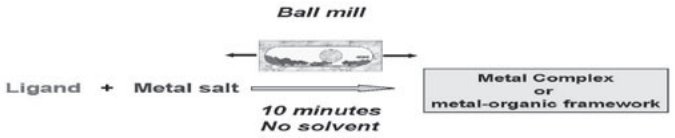
Acta Cryst. (2008). A**64**, C40

Mechanochemical solvent-free synthesis of metal-organic frameworks

Stuart L James
Queen's University Belfast, Chemiatry and Chemical Engineering, David Keir Building Stranmillis Road, Belfast, Northern Ireland, BT9 5AG, UK, E-mail：s.james@qub.ac.uk

Simply grinding together metal salts and organic bridging ligands, in the absence of solvent in a shaker mill can provide crystalline, microporous metal-organic frameworks in only a few minutes and in quantitative yield[1]. Systematic studies of this unusual type of synthesis will be presented, including microscopy, structural templation by guests and by-products, the formation of interpenetrated structures, structures based on mixed-ligands, and the sorption characteristics of the resulting products.

[1] Solvent-free synthesis of a microporous metal-organic framework, A. Pichon, A. Lazuen-Garay and S.L. James CrystEngComm 2006, 8, 211.



Keywords: reactivity, mechanochemistry, metal-organic complexes

MS.18.1

Acta Cryst. (2008). A**64**, C40

Application of the pair-distribution-function method to *in-situ* studies in catalysis

Peter J Chupas
Argonne National Laboratory, X-ray Science DIvision, 9700 South Cass Ave. Building 433, Argonne, IL, 60439, USA, E-mail：chupas@anl.gov

Recent advances in PDF measurements combining 2-dimensional area detectors and high-energy (>60 keV) X-rays have dramatically decreased measurement times for high resolution PDF (Pair-Distribution-Function) measurements to times as fast as 30 milliseconds. This time-resolution has opened up the possibility of time-resolved and in-situ measurements. Specifically this talk will cover the application of time-resolved PDF measurements to investigate the mechanism and kinetics of formation of catalytic nano-particles. Recent work investigating the formation of highly-dispersed supported metal nano-particles with time-resolved PDF will be discussed. Pivotal to the development of catalytic materials with controlled reactivity, is the understanding of the fundamental mechanisms that drive the formation of catalytic nano-particles. A key step towards this goal is the ability to discriminate between the separate processes including the initial reaction of the precursors and the subsequent nano-particle sintering. Here we use time-resolved PDF methods to monitor the structural evolution and kinetics associated with the formation of Pt(0) nano-particles from Pt(4+). Differential-PDF (d-PDF) methods are applied, which allow the atom-atom correlations involving Pt to be separated from those of the support material (TiO_2), to probe the structure of the nano-particles directly. The application of d-PDF methods to the study the structure of the complexes that molecules form when bound to catalysts will also be discussed.

Keywords: catalysis, pair-distribution-function, *in-situ* structural studies

MS.18.2

Acta Cryst. (2008). A**64**, C40

In situ studies on hydrogen/ammonia storage materials

Kenny Stahl, Rasmus Z Sorensen, Claus H Christensen
Technical University of Denmark, Department of Chemistry, Building 207, Lyngby, N/A, DK-2800, Denmark, E-mail：kenny@kemi.dtu.dk

$Mg(NH_3)_6Cl_2$ is a new promising hydrogen storage material. It already fulfils the U.S. DOE goals for 2015 in terms of gravimetric and volumetric hydrogen density, and energy density. On mild heating this material releases four to six NH_3 that can be used directly in some fuel cells or in deNOx-processes. Alternatively, NH_3 can be decomposed into N_2 and H_2 prior to use in standard fuel cells. For the present study $Mg(NH_3)_6Cl_2$ was sealed in quartz capillaries and studied in situ with X-ray synchrotron powder diffraction under varying temperature at beamline I711, MAXlab, Lund, Sweden. The experiments showed that under autogenous pressure, $Mg(NH_3)_6Cl_2$ loses four NH_3 before melting at 600 K. Repeated temperature cycling between 323 and 453 K demonstrated that the process is essentially reversible, but some $Mg(NH_3)_2Cl_2$ is retained at 323 K under transformation to a low-temperature phase. Below approximately 300 K it reverts completely to $Mg(NH_3)_6Cl_2$. Analogous studies of related materials $Ni(NH_3)_6Cl_2$ and $Cu(NH_3)_5SO_4$ showed different deammination sequences: $Ni(NH_3)_6Cl_2$ transforms to $Ni(NH_3)_2Cl_2$ at 450 K, to $Ni(NH_3)Cl_2$ at 575 K, and to pure nickel metal at 700 K. Returning to room temperature the sample reverts to a mixture of $Ni(NH_3)_xCl_2$-phases. $Cu(NH_3)_5SO_4$ showed transformations to $Cu(NH_3)_4SO_4$ at 373 K, to $Cu(NH_3)_2SO_4$ at 450 K, and to $Cu(NH_3)SO_4$ at 550 K. Repeated cycling between 323 and 523 K showed complete reversibility between $Cu(NH_3)_5SO_4$ and $Cu(NH_3)_2SO_4$. The experimental results, crystal structures and structure relationships will be presented and discussed.

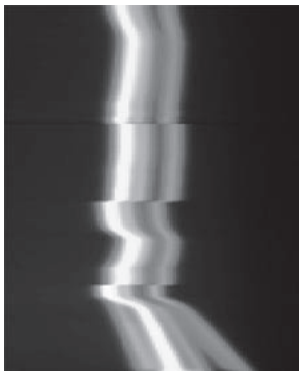
Keywords: *in situ* powder diffraction, energy storage materials, structural relationships

MS.18.3

Acta Cryst. (2008). A**64**, C40−41

In situ synchrotron powder X-ray diffraction studies of catalytic materials

Poul Norby
University of Oslo, Department of Chemistry and Centre for Materials Research and Nanotechnology, P.O. Box 1033, Olso, Oslo, 0315, Norway, E-mail：poul.norby@kjemi.uio.no



Development of in situ powder diffraction methods has made a significant impact in materials science. Particularly utilization of synchrotron X-ray radiation has greatly improved the ability to investigate materials under operative or realistic working conditions or during synthesis. Information extracted from diffraction experiments may contribute to the understanding of catalytic processes and the

catalytic material under operative conditions. To recreate actual conditions in a catalytic reactor, and to be able to study many catalytic processes, require a robust and flexible system. We have developed a facility at the Swiss-Norwegian beam lines (SNBL) at the European Synchrotron radiation Facility (ESRF), where operating (flow) conditions up to 20 atm. and 900C in variable and switchable gas mixtures may be achieved. The system will be used for in situ powder diffraction as well as for XAS studies. A mass spectrometer is available for analysis of exhaust gases and a Raman spectrometer has been installed for combined in situ experiments. Results from studies of catalytic materials at operating conditions will be given.

Keywords: *in situ*, catalysis, operating conditions

MS.18.4

Acta Cryst. (2008). A**64**, C41

In situ simultaneous Raman/XRPD study of solid-state reactions at non-ambient conditions

Marco Milanesio[1], Davide Viterbo[1], Enrico Boccaleri[1], Wouter van Beek[2]

[1]Universita del Piemonte Orientale, Dipartimento di Scienze e Tecnologie Avanzate, Via Bellini 25/G, Alessandria, AL, I-15100, Italy, [2]Swiss-Norwegian Beamlines, ESRF, BP 220, F-38043 Grenoble Cedex, France., E-mail：marco.milanesio@mfn.unipmn.it

Materials containing disordered moieties and/or amorphous or liquid-like phases or showing surface- or defect-related phenomena constitute a problem for their characterization using X-ray powder diffraction (XRPD), and in many cases Raman spectroscopy can provide useful complementary information. We have designed and realized a novel experimental set-up for simultaneous in situ Raman/High-resolution XRPD experiments to take full advantage of the complementarities of the two techniques in investigating solid-state transformations at non-ambient conditions. The invaluable added value of the proposed experiment is the perfect synchronization of the two probes with the reaction coordinate and the elimination of possible bias caused by different sample holders and conditioning modes used in *in-situ* but separate approaches. A gas blower allows studies from RT to 700K and 100K can be reached using a nitrogen cryostream. The experimental setup flexibility allows the addition of ancillary devices, such as a UV-lamp used to study photoreactivity or DAC to study high pressure regime. The set-up was tested on three solid-state transformations: i) the kinetics of the fluorene:TCNQ solid-state synthesis, ii) the thermal swelling and degradation of stearate-hydrotalcite nanocomposites, iii) the photoinduced 2+2 cyclization of (E)-furylidenoxindole. The reported experiments demonstrated that, even though the simultaneous Raman/XRPD experiment is more challenging than the separated ones, high resolution XRPD and Raman data can be collected. Concerning the obtained results, Raman gave information on surface reactivity and on flexible and disordered organic moieties hydration states while XRPD gave information on bulk properties and on stiff inorganic moieties.

Keywords: *in-situ* time-resolved powder diffraction, reaction mechanisms, raman spectroscopy

MS.18.5

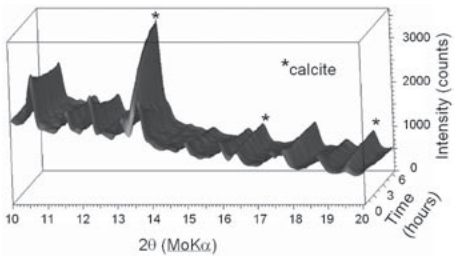
Acta Cryst. (2008). A**64**, C41

Application of a high-pressure CO_2 cell to time-resolved studies with a lab powder diffractometer

Pamela S Whitfield, Lyndon D Mitchell, Arghavan V Nawaby, Isobel J Davidson

National Research Council Canada, Institute for Chemical Process and Environmental Technology, Building M12, 1200 Montreal Road, Ottawa, Ontario, K1A 0R6, Canada, E-mail：pamela.whitfield@nrc.gc.ca

A gas-cell design for laboratory diffractometers rated to 12.4 MPa and 200 ℃ has been certified and constructed to the latest pressure vessel design codes [1]. The gas of interest in this case is CO_2 which is supercritical above 7.4 MPa and 31℃. The temperature/pressure behaviour of CO_2 adds significant complications to the experimental application. The cell has been coupled with MoKα radiation and the Bruker Vantec PSD to enable time resolved studies to be conducted on a laboratory diffractometer. The snap-shot mode of the detector has been used to study the crystallization of poly-lactic acid (PLA) and PLA-clay composites under CO_2 pressure. Additionally, the carbonation of wollastonite has been studied as an initial model system for potential application to CO_2 sequestration studies. Given the sluggish kinetics of many sequestration reactions under milder conditions, restricted beamtime allocations at synchrotrons could be seen as a practical disadvantage for comprehensive studies versus a laboratory diffractometer.



[1] Whitfield, P.S., Nawaby, A.V., Blak, B., & Ross, J., J.Appl.Cryst, v41 (2008), 350-355

Keywords: gas-solid reactions, *in-situ* powder diffraction, time-resolved powder diffraction

MS.19.1

Acta Cryst. (2008). A**64**, C41−42

Evolutionary crystal structure prediction and its applications to materials at extreme conditions

Artem R. Oganov[1,2], Mario Valle[3], Andriy Lyakhov[1], Yanming Ma[1,4], Yu Xie[1,4]

[1]ETH Zurich and Moscow State University, Materials, Wolfgang-Pauli-Strasse 10, Zurich, Switzerland, 8093, Switzerland, [2]Moscow State University, 119992 Moscow, Russia, [3]CSCS, Galleria 2, via Cantonale, Manno 6928, Switzerland, [4]National Lab of Superhard Materials, Jilin University, Changchun 130012, P. R. China, E-mail：a.oganov@mat.ethz.ch

Crystal structure prediction on the basis of just the chemical formula has long been considered a formidable or even insoluble problem. Several methods have recently been proposed to tackle this problem, among which the evolutionary algorithm USPEX (Universal Structure Predictor: Evolutionary Xtallography [1-3]) proved to be particularly efficient and reliable. Key ingredients of this method (selection, variation operators, redundancy control and constraint techniques) and its current developments will be discussed. Applications of this methods so far are quite numerous and include several technologically important systems and many materials of mainly fundamental interest (high-pressure phases of hydrogen,